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B 08 B 3/10		Z-6420-3B	

審査請求 未請求 発明の数 1 (全3頁)

⑭発明の名称　半導体ウエハの洗浄方法

⑳特　願　昭60-258064
㉒出　願　昭60(1985)11月18日

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typ 80-100°C
Sgn
and

2

明　細　書

1. 発明の名称　半導体ウエハの洗浄方法

2. 特許請求の範囲

(1) アンモニア、硫酸、塩酸等より成る洗浄液内に半導体ウエハを浸漬した後、前記洗浄液中にオゾンを供給することを特徴とする半導体ウエハの洗浄方法。

3. 発明の詳細な説明

(イ) 産業上の利用分野

本発明は半導体ウエハの洗浄方法、特に洗浄中に酸素を供給する半導体ウエハの洗浄方法に関する。

(ロ) 従来の技術

従来、半導体ウエハの洗浄方法としては第2図に示す如く、洗浄槽01内に硫酸(H_2SO_4)、アンモニア水(NH_4OH)、塩酸(HCl)、弗酸(HF)等の10%以下の希釈液を洗浄液02として入れ、この洗浄液02をヒーター03で80℃程度に加熱し、この液02内に半導体ウエハを浸漬して洗浄を行っている。洗浄の活性化を行うために半導体ウエハの投入直前に過酸化水素(H_2O_2)を洗浄液02に滴下して酸素を発生させて洗浄の均一化を図っている。

斯る方法は例えば特開昭59-46032号公報(H01L21/304)等で公知である。

(ハ) 発明が解決しようとする問題点

しかしながら斯上の方法では種々の欠点が生じた。第1に過酸化水素を用いるため熱分解されて水が発生し、洗浄液02が更に希釈され洗浄にむらが生じて半導体ウエハの表面均一性が悪い欠点があった。このため熱酸化による酸化膜の欠陥密度が高くなったり、ポリシリコンの洗浄では表面状態にむらが生じる。

第2に過酸化水素を用いるためその液内に含まれるゴミで洗浄液02が汚れ、クリーンな洗浄を行なえない欠点があった。

第3に洗浄液02の温度を上昇して洗浄効率を上げようとすると過酸化水素の熱分解が速められてかえって洗浄効果が落ちる欠点があった。

(ニ) 問題点を解決するための手段

本発明は所上した欠点に鑑みてなされ、洗浄液中にオゾンを供給することにより従来の欠点を大巾に改　した半導体ウェハの洗浄方法を提供するものである。

(ii)　作用

本発明に依れば、洗浄時間中洗浄液(4)中にオゾンガスを注入しているので、酸素を一定量供給でき洗浄液(4)の希釈化も防止できる。

(iii)　実施例

本発明に依る半導体ウェハの洗浄方法を第１図を参照して詳述する。

洗浄槽(1)内に９０～９６％の濃硫酸原液（H_2SO_4）、アンモニア水（NH_4OH）、塩酸（HCl）、硝酸（HNO_3）、弗酸（HF）等の１０％以下の希釈液を洗浄液(4)として入れ、この洗浄槽(1)下に多孔を有する石英又はテフロンより成るパイプ(2)を設けてオゾン（O_3）が下から吹き出す様になっている。洗浄槽(1)の下にはヒーター(3)を設け、洗浄液(4)を加熱する。硫酸の場合は１００～１４０℃に加熱し、アンモニア水の場合は８０～１００℃に加熱している。

斯る洗浄槽(1)内に治具に収納した半導体ウェハを浸漬し、パイプ(2)よりオゾンを注入して酸素イオンを洗浄液(4)内に供給しながら半導体ウェハの洗浄を行う。

斯る方法に依れば、オゾンが気体であるので洗浄液(4)の希釈化を伴なわずに酸素イオンを供給し続ける。これにより洗浄表面の酸化を促進して親水処理を行なえるので極めてクリーンな洗浄を安定して行なうことができる。

第３図に本発明と従来の洗浄方法の洗浄効果を説明する特性図を示す。従来ＲＣＡ洗浄法と呼ばれている$NH_4OH+H_2O_2$と本発明のNH_4OH+O_3とを比較すると、従来では加熱温度がH_2O_2の熱分解より８０～９０℃に限られ、$H_2O_2 \rightarrow H_2O+O^{\bullet}\uparrow$の熱分解により発生する水により液希釈が生じて矢印の様に洗浄効果が劣化しているのに対し、本発明ではオゾンを用いるため１００℃以上に加熱でき洗浄効果を大巾に向上できる。また従来の$H_2SO_4+H_2O_2$と本発明の

$H_2SO_4+O_3$についても同様の効果が得られる。

(iv)　発明の効果

本発明に依れば、第１にオゾンを酸素イオン発生源として用いるので洗浄液(4)が希釈化されず、酸素イオンで洗浄が活性化され半導体ウェハの表面を均一に且つ安定して洗浄できる利点を有する。

第２にオゾンは気体であるので注入しても洗浄液(4)がゴミ等で汚染されるおそれがなくなり、クリーンな洗浄ができる利点を有する。

第３にオゾンを用いるので洗浄液(4)の温度をH_2O_2の熱分解に無関係に上げても酸素イオンを一定量供給でき、洗浄効果を従来の２倍以上に向上できる利点を有する。

第４にオゾンを用いるのでH_2O_2を用いる場合に比べてH_2O_2の液の管理が不要となり安全上の管理が容易となる利点を有する。

4.　図面の簡単な説明

第１図は本発明に依る半導体ウェハの洗浄方法を説明する断面図、第２図は従来の半導体ウェハ

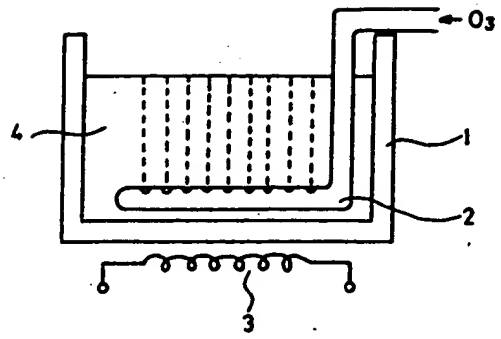
の洗浄方法を説明する断面図、第３図は本発明と従来の洗浄効果を説明する曲線図である。

(1)は洗浄槽、(2)はパイプ、(3)はヒーター、(4)は洗浄液である。

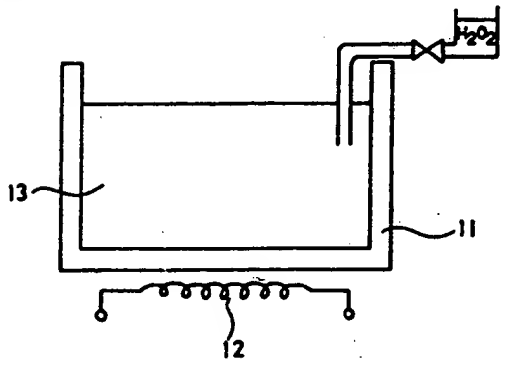
出願人　三洋電機株式会社　外１名

代理人　弁理士　　佐　野　静　夫

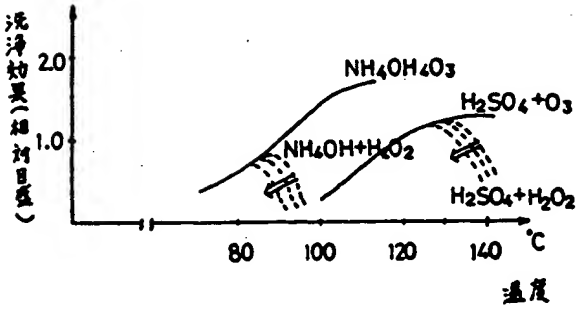
第 1 図


O3
4
1
2
3

第 2 図


H2O2
13
11
12

第 3 図


洗浄効果(相対目盛)
2.0
1.0
NH4OH+O3
H2SO4+O3
NH4OH+H2O2
H2SO4+H2O2
80
100
120
140
℃
温度

NON-CERTIFIED, UNFORMATTED TRANSLATION FROM INTERLIN UA.COM

WADA et al

Reference No.
Job N . TOT-LYON-2268A

19. Japan Patent Office (JP) 11. Patent Application Laid-open No.

12. Japan Laid-open Patent Gazette (A) Showa 62-117330(1987)

51. Int. Cl.[3]	ID Code	Internal Reference No.	43. Patent Laid-open Date: May 28, 1987 (Showa 62)
H 01 LJ 21/304		D-7446-4F	Place for Technology Labeling
B 08 B 21/304		Z-6420-3B	

Request for Examination: Attached / Not Requested Number of Claims: 1 (Total 3 pages)

54. Title of Invention	Semiconductor Wafer Cleaning Method
21. Application No.	Showa 60-258064
22. Date of Filing	November 18, 1985 (Showa 60)
72. Inventor	Toshio Wada 18, Oaza-Sakada, Oizumi-cho, Ouragun, Gunma-ken Tokyo Sanyo Electric Co., Ltd
72. Inventor	Norio Koide 18, Oaza-Sakada, Oizumi-cho, Ouragun, Gunma-ken Tokyo Sanyo Electric Co., Ltd
71. Applicant	Sanyo Electric Co., Ltd 2-18, Keihan-hondori, Moriguchi-shi, Osaka
71. Applicant	Tokyo Sanyo Electric Co., Ltd 18, Oaza-Sakada, Oizumi-cho, Ouragun, Gunma-ken
74. Agent	Takushi 'Nishino, Patent Attorney, and one additional person

SPECIFICATION

1. Title of the invention Semiconductor Wafer Cleaning Method

2. Claims

(1) A semiconductor wafer cleaning method, characterized in that a semiconductor wafer is immersed in a cleaning liquid composed of ammonia, sulfuric acid, hydrochloric acid or other substance, whereupon ozone is supplied to the aforementioned cleaning liquid.

3. Detailed description of the invention

Field of industrial utilization

The present invention concerns a method for cleaning semiconductor wafers, and in particular, concerns a method for cleaning semiconductor wafers wherein oxygen is supplied during cleaning.

Prior art

In the past, methods for cleaning semiconductor wafers, as shown in Figure 2, have involved introducing a dilute solution containing 10% or less of such substances as sulfuric acid (H_2SO_4), aqueous ammonia (NH_4OH), hydrochloric acid (HCl) and hydrofluoric acid (HF) into a cleaning vessel 11, and heating this cleaning liquid 13 to approximately 80°C with a heater 12. The semiconductor wafer is cleaned by immersing it in this liquid 13. In order to improve the cleaning activity, hydrogen peroxide (H_2O_2) is added dropwise to the cleaning liquid 13 immediately prior to introduction of the semiconductor wafer so that oxygen is generated, thereby achieving greater cleaning uniformity.

' ILS Note – An alternative way of reading this person's name is Hiroshi.

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This type of method is common knowledge in, for example, Japanese Unexamined (Kokai) Patent Application No. Sho 59-46032 (H 01 L 21/304).

Problems to be solved by the invention

However, various disadvantages have resulted from the type of method described above. Firstly, there is the disadvantage that water is generated due to thermal decomposition resulting from the use of hydrogen peroxide, and the cleaning liquid 13 is thus additionally diluted, producing non-uniform cleaning which results in a loss of surface uniformity of the semiconductor wafer. For this reason, the defect density of oxide films formed by thermal oxidation increases, and the surface condition becomes non-uniform during polysilicon cleaning.

Secondly, there is the disadvantage that the cleaning liquid 13 is contaminated by contaminants contained in the liquid because hydrogen peroxide is used, so that a clean cleaning process is not carried out.

Thirdly, if the attempt is made to improve cleaning efficiency by increasing the temperature of the cleaning liquid 13, there is the disadvantage that thermal decomposition of the hydrogen peroxide will accelerate, and the cleaning effects will actually be compromised.

Means for solving the problems

The present invention was developed in light of the disadvantages described above, and offers a cleaning method for semiconductor wafers wherein past disadvantages have been dramatically mitigated by means of supplying ozone to the cleaning liquid.

Action

In accordance with the present invention, ozone gas is introduced into the cleaning liquid 4 during cleaning, so that oxygen can be supplied in constant quantities and dilution of the cleaning liquid 4 can be stopped.

Working examples

The cleaning method for semiconductor wafers pertaining to the present invention is described below in reference to Figure 1.

A 90-96% concentrated sulfuric acid stock solution (H_2SO_4), ammonia aqueous solution (NH_4OH), hydrochloric acid (HCl), nitric acid (HNO_3) or hydrofluoric acid (HF) is diluted to 10% or less and is introduced as cleaning liquid 4 into a cleaning vessel 1, where a pipe 2 composed of quartz or Teflon is installed below the cleaning vessel 1 in such a manner that ozone (O_3) is blown upwards from below. A heater 3 is installed below the cleaning vessel 1 for heating the cleaning liquid 4. With sulfuric acid, heating is performed at 100-140°C, whereas with ammonia aqueous solution, heating is performed at 80-100°C.

A semiconductor wafer that is held on a stand is immersed in this cleaning vessel 1, and ozone is introduced from the pipe 2 so that the semiconductor wafer is cleaned while supplying oxygen ions into the cleaning liquid 4.

In this method, oxygen ions are continuously supplied without accompanying dilution of the cleaning liquid 4 because ozone is a gas. By this means, oxidation of the cleaned surface is facilitated and a hydrophilic treatment is carried out, so that an extremely clean cleaning process can be performed with good reliability.

Characteristic curves used for representing cleaning effects in the cleaning method of the present invention and a conventional cleaning method are shown in Figure 3. In comparing the method of the present invention wherein $NH_4OH + O_3$ is used and a method known as a conventional RCA cleaning method wherein $NH_4OH + H_2O_2$ is used, the heating temperature has been restricted to 80-90°C in the past due to thermal decomposition of the H_2O_2, and the cleaning effects deteriorate as indicated by the arrow due to dilution of the liquid with water generated by thermal decomposition: H_2O_2 //arrow// $H_2O + O$*//upwards arrow//. With the present invention, however, ozone is used so that cleaning effects are greatly improved because heating can be performed at 100°C or greater. In addition, the method of the present invention that employs $H_2SO_4 + O_3$ provides effects that are similar to those of conventional methods that employ $H_2O_4 + H_2O_2$.

Effect of the invention

Firstly, the present invention has the advantage that ozone is used as the source for generating oxygen ions, so that the cleaning liquid 4 is not diluted, and cleaning is activated by the oxygen ions. As a result, cleaning can be reliably and uniformly carried out at the surface of the semiconductor wafer.

Secondly, the invention has the advantage that ozone is a gas, and thus there is no danger of pollution of the cleaning liquid 4 with contaminants when this substance is introduced, so that cleaning can be performed

without contamination.

Thirdly, the invention has the advantage that, because ozone is used, oxygen ions can be supplied in constant amounts even if the temperature of the cleaning liquid 4 is increased, because there is no connection with thermal degradation of H_2O_2. The cleaning effects can thus be increased by two or more times over past methods.

Fourthly, the invention has the advantage that, because ozone is used, H_2O_2 liquid need not be managed, which simplifies management from the standpoint of safety relative to cases where H_2O_2 is used.

Brief description of the figures

Figure 1 is a cross-sectional diagram describing the cleaning method for semiconductor wafers pertaining to the present invention, Figure 2 is a cross-sectional diagram describing a conventional method for cleaning semiconductor wafers, and Figure 3 is a graph for showing the cleaning effects obtained in the past and with the present invention.

1 Cleaning vessel
2 Pipe
3 Heater
4 Cleaning liquid

Figure 1

Figure 2

Figure 3
1 Cleaning effects (relative scale)
2 Temperature

-9- (WPAT)
AN - 87-117330
TI - WASHING METHO R SEMICONDUCTOR WAFER
PA - (2000188) SA ELECTRIC CO LTD
IN - WADA, TOSHIO; KOIDE, NORIO
PN - 87.05.28 062117330, JP 62-117330 A
AP - 85.11.18 85JP-258064, 60-258064
SO - 87.10.27 SECT. E, SECTION NO. 552; VOL. 11, NO. 329, PG. 141.
IC - H01L-021/304; B08B-003/10
JC - 42.2 (ELECTRONICS--Solid State Components); 28.1 (SANITATION--Sanitary Equipment)
AB - PURPOSE: To wash a wafer surface uniformly and stably without diluting a washing by injecting ozone gas into the washing during the washing time. CONSTITUTION: A diluted solution, such as 90-96% H(sub 2)SO(sub 4), NH(sub 4)OH, HCl, etc. is introduced into a washing tank 1 as a washing 4 while a pipe 2 consisting of quartz, Teflon, etc. with a large number of holes is mounted to a lower section in the tank 1 and ozone can be fed. A heater 3 is installed to the lower section of the tank 1, and the liquid 4 is heated. Semiconductor wafers housed in a jig are dipped into the tank 1, ozone is injected from the pipe 2, and the semiconductor wafers are washed, feeding oxygen ions to the liquid 4. Accordingly, since ozone is a gas, the liquid 4 is not diluted, and the oxidation of a washing surface is accelerated and hydrophilic treatment is executed, thus stably conducting extremely clean washing.

SS 24?

$H_2SO_4 - H_2O - O_3$
$NH_4OH - H_2O - O_3$ or
$HCl - H_2O - O_3$ or

-9- (WPAT)
AN - 87-188360/27
TI - Appts. for cleaning semiconductor wafer - supplies ozone into washings composed of ammonia, sulphuric acid, and hydrochloric acid during cleaning NoAbstract Dwg 1/3
DC - L03 P43 U11
PA - (SAOL) SANYO ELECTRIC CO; (TOKR) TOKYO SANYO ELECTRIC CO
PR - 85.11.18 85JP-258064
NUM - 1 patent(s) 1 country(s)
PN -- JP62117330 A 87.05.28 (8727) 8p
AP -- 85JP-258064 85.11.18
IC2 - B08B-003/10 H01L-021/30

102- 82-85, 88-90

JP